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Photoluminescence properties of a novel phosphor, Na₃La₉O₃(BO₃)₈: $RE^{3+}(RE = Eu, Tb)$

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Abstract

The new oxyborate phosphors, Na₃La₉O₃(BO₃)₈:Eu³⁺ (NLBO:Eu) and Na₃La₉O₃(BO₃)₈:Tb³⁺ (NLBO:Tb) were prepared by solidstate reactions. The photoluminescence characteristics under UV excitation were investigated. The dominated emission of Eu³⁺ corresponding to the electric dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ is located at 613 nm and bright green luminescence of NLBO:Tb attributed to the transition ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ is centered at 544 nm. The concentration dependence of the emission intensity showed that the optimum doping concentration of Eu and Tb is 30% and 10%, respectively.

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1. Introduction

Rare-earth-activated phosphors have attracted much attention for their well-defined transitions within the 4*f* shell [1]. Eu³⁺ is an excellent activator for the red-emitting phosphor, and Tb³⁺ for the green-emitting. Eu³⁺-or Tb³⁺-doped borate phosphors have been extensively studied in the past decades. The borates are good candidates as the host lattices for luminescence because of their large band gap [2–6]. For example (Y,Gd)BO₃:Eu is widely used in plasma display panel applications [7–9]. And YBO₃:Tb³⁺ prepared by hydrothermal synthesis is a promising phosphor for plasma display panels and hydrargyrum-free lamps [10,11]. SrBPO₅-related phosphors (SrBPO₅:Tb³⁺,Ce³⁺ and Na⁺) exhibit enhanced luminescence and can be utilized as green phosphors in tricolor lamps [12].

In 2001, a new sodium lanthanum oxyborate, Na₃ La₉O₃(BO₃)₈(NLBO), was obtained by Wu et al. [13]. Gravereau et al. [14] reported the preparation of the single crystal and solved its crystal structure. It belongs to the hexagonal system with space group *P*-62*m*. Its basic

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structure is composed of BO3 planar triangle, LaO9 polyhedra, LaO₈ polyhedra, and NaO₆ polyhedra. The first nearest La-La distance and the second nearest La-La distance in the structure is 3.691 and 4.030 Å, respectively [15]. Generally, a weak crystal field may be expected at the rare-earth sites due to the high degree of covalency in the BO₃ anions, while larger interatomic distance reduces exchange coupling and multipolar interactions. These are in agreement with a requirement for weak concentration quenching [16]. It is worthwhile therefore to study the luminescence properties of active rare-earth ions in new oxy borate Na₃La₉O₃(BO₃)₈. To our knowledge, photoluminescence (PL) properties of NLBO: RE^{3+} (RE = Eu, Tb) under ultraviolet (UV) excitation have not been reported. In this paper, we report the preparation of NLBO: RE^{3+} (RE = Eu, Tb) and their luminescent characteristics in UV region.

2. Experiment

 Eu^{3+} -doped NLBO was synthesized by solid-state reactions. The stoichiometric amount of starting materials Na₂CO₃(A.R.), H₃BO₃(A. R.), La₂O₃(99.99%) and Eu₂O₃(99.99%) were mixed in an agate mortar, except

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for H₃BO₃(A.R.) with excess of 3–5% to compensate the evaporation. The mixtures were ground thoroughly and preheated at 500 °C for 10 h. Cooled and reground, then heated at 1055 °C for 24 h twice with the intermediate grindings to obtain the phosphor samples. In preparation of Tb³⁺-doped NLBO, we used Tb₄O₇ (99.99%) instead of Eu₂O₃(99.99%).

The samples were characterized by an X-ray powder diffractometer (Bruker D8 ADVANCE) with Cu $K\alpha$ radiation. PL spectra were conducted using a fluorescence spectrometer (Hitachi F-4500). The measurements were all performed at room temperature.

3. Results and discussion

Fig. 1 shows the XRD pattern of NLBO: $Eu^{3+}(30\%)$ and NLBO: $Tb^{3+}(10\%)$ in the range of 2θ from 5° to 70°. They both agree with the XRD pattern of NLBO crystal [17] and there is no second phase observed. We calculate the cell parameters of different doping concentrations for Eu^{3+} and Tb^{3+} as shown in Table 1. With the increase of doping concentration, diffraction peaks slightly shift to higher angle. Because the radius of Eu^{3+} (0.950 Å) and Tb^{3+} (0.923 Å) is close to that of La^{3+} (1.061 Å), Eu^{3+} and Tb^{3+} can be easily doped into host lattice and substituted for the site of La^{3+} ions. We conclude that rare-earth doping does not destroy the lattice frame of NLBO, and Eu^{3+} or Tb^{3+} has been efficiently incorporated into the host lattice.

The excitation and emission spectra of NLBO: Eu^{3+} (30%) are shown in Fig. 2. The broad band in 220–300 nm region originates from the charge-transfer transition of $O^{2-} \rightarrow Eu^{3+}$, and the other sharp lines in the range of 300–500 nm correspond to the *f*-*f* transitions of Eu^{3+} ions.

The right part in Fig. 2 presents the emission spectrum of NLBO:Eu³⁺ excited at 395 nm. From 550–750 nm there are groups of sharp lines assigned to the transitions of ${}^{5}D_{0}$ to ${}^{7}F_{J}$ (J = 1, 2, 3, 4) levels of Eu³⁺ activators. The



Fig. 1. XRD pattern of NLBO:Eu³⁺(30%) and NLBO: Tb³⁺(10%).

Table 1	
The cell j	parameters of NLBO:Eu ³⁺ and NLBO:Tb ³⁺

	a (Å)	<i>c</i> (Å)
Concentration of 1	$Eu^{3+}(\%)$	
5	8.853(7)	8.615(6)
10	8.840(0)	8.619(7)
15	8.819(4)	8.558(5)
20	8.791(3)	8.476(6)
25	8.772(2)	8.452(4)
30	8.777(9)	8.459(1)
35	8.769(6)	8.492(3)
Concentration of 2	Tb^{3+} (%)	
5	8.861(6)	8.652(0)
10	8.813(1)	8.520(9)
15	8.794(2)	8.527(2)
20	8.781(7)	8.527(1)



Fig. 2. Excitation and emission spectra of NLBO:Eu³⁺(30%).

emission peaks at around 654 and 700 nm correspond to the transition ${}^{5}D_{0} \rightarrow {}^{7}F_{3,4}$. The dominated red emission ranging from 610 to 630 nm (613, 622, 628 nm) is attributed to the electric dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$, indicating that Eu^{3+} is located at the site of non-inversion symmetry [18]. The emission at 589 and 598 nm originates from the magnetic dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$. There is one weak emission peak at 579.4 nm due to the electric dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$, which is forbidden and sensitive to the crystal field [19]. The ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition exists only when Eu^{3+} occupies sites with local symmetries of C_n , C_{nv} or C_s and the number of emission peaks from ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition equals the number of site of Eu^{3+} with C_n , C_{nv} or C_s symmetry. So we can deduce that Eu^{3+} occupies one site of C_n , C_{nv} or C_s symmetry.

The structure of NLBO is characterized by alternate stacking along the *c*-axis of Na–B–O, B–O, La and La–O containing layers with a mirror plane at z = 1/2. A framework of La₉O₃ rings and rows of BO₃ triangles running along the *c*-direction is established. Each La₉O₃ ring is constituted of three La₄O tetrahedra sharing a

common La corner. In the structure, La^{3+} ion has two types of coordinations: La1O₈ (La1 in 3g) and La2O₉ (La2 in 6i) [14,20]. The symmetry of La³⁺ is C_{2v} and C_s , respectively (Fig. 3). Because the crystal structure offers two different sites for lanthanum, Eu³⁺ may replace either La1 with the symmetry of C_{2v} , or else La2 with the symmetry of C_s .

The electrical dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ is hypersensitive to the local environment, while the magnetic dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ is not affected much by the ligand field around the Eu³⁺. Therefore the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}/{}^{5}D_{0} \rightarrow {}^{7}F_{1}$ intensity ratio(R/O value) is a measure of the rare-earth ion site symmetry. A lower symmetry of the crystal field around Eu³⁺ will result in a higher R/O value [21]. When the intensities of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ are comparable, the features imply a higher site-symmetry of Eu³⁺ [22]. For NLBO:Eu³⁺ the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}/{}^{5}D_{0} \rightarrow {}^{7}F_{1}$ intensity ratio(R/Ovalue) is 1.26. It is deduced that Eu³⁺ replace La1 with the symmetry of C_{2v} . So only one ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition is observed.

As shown in Fig. 4 the excitation spectrum of NLBO:Tb³⁺(10%) is a broad band in 230–300 nm range from the $4f^8 \rightarrow 4f^75d^1$ transition of Tb³⁺ and many weak peaks in 300–400 nm range from the $4f \rightarrow 4f$ transition of

Tb³⁺. This type of behavior is also observed in many Tb³⁺-doped materials, for example CaYBO₄:Tb [23], CaLaP₃O₁₀:Tb [24] and SrAl₂B₂O₇:Tb [25]. Right part in Fig. 4 exhibits the emission spectrum of Tb³⁺-doped NLBO excited at 257 nm. It consists of typical Tb³⁺ emission due to the ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ (J = 6,5,4,3) transition, which are ${}^{5}D_{4} \rightarrow {}^{7}F_{6}(483, 490, 493 \text{ nm})$, ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ (544, 555 nm), ${}^{5}D_{4} \rightarrow {}^{7}F_{4}(585, 590 \text{ nm})$, ${}^{5}D_{4} \rightarrow {}^{7}F_{3}$ (621, 627 nm), respectively. Among them the emission at 544 nm is the strongest.

We record the relative intensity of NLBO:Eu at 613 nm and NLBO:Tb at 544 nm as functions of doping concentrations. Concentration dependence of the emission intensity is shown in Fig. 5. Because of concentration quenching, the emission intensity increases, and then decreases. NLBO:Eu and NLBO:Tb exhibited weak concentration quenching and the quenching concentration is 30% for NLBO:Eu and 10% for NLBO:Tb. This is possibly attributed to the high degree of covalency of BO₃ anions and larger interatomic distance of rare-earth ions in Na₃La₉O₃(BO₃)₈ structure.



Fig. 3. Coordination polyhedra of the La1, La2 cations [14,20].



Fig. 4. Excitation and emission spectra of NLBO:Tb³⁺(10%)



Fig. 5. Concentration dependence of the emission intensity of (a) NLBO:Eu (b) NLBO:Tb.

4. Conclusions

Na₃La₉O₃(BO₃)₈:Eu³⁺ (NLBO:Eu) and Na₃La₉O₃ (BO₃)₈:Tb³⁺ (NLBO:Tb) have been synthesized by solidstate reaction. PL spectra show that the dominated emission of NLBO:Eu located at 613 nm is from the electric dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ and the emission at 589 and 598 nm originates from the magnetic dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$. We can deduce that Eu³⁺ is located at the site of non-inversion symmetry and Eu³⁺ is substituted for La1 with the symmetry of C_{2v} . NLBO:Tb emit bright green luminescence centered at 544 nm attributed to the transition ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$. Na₃La₉O₃(BO₃)₈: $RE^{3+}(RE = Eu,Tb)$ may be a novel choice as phosphor material for lamps and display applications.

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